The Catalytic Reduction of Nitrogen Oxide by Carbon Monoxide over Metal Oxide Catalysts —The Correlation of the Activities with the Surface States of Metal Oxides—

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(Received July 21, 1975)

In the catalytic NO–CO reaction over metal oxide catalysts, the surface states of reduced metal oxides were studied with ESCA, and the correlation of the activities of the reduced metal oxide catalysts for the NO–CO reaction with their surface states was investigated. The surfaces of the catalysts were studied with ESCA after treatments *in situ*. It was revealed that the surface states of the metal oxides did not always agree with their bulk constituents. For example, it was found that the oxygen in the surface layer of the cobalt oxide after a proper reduction treatment by CO was richer than in its bulk. Moreover, the correlation between the surface states and the activities of those oxides was successfully explained. It was also concluded that, in the NO–CO reaction, the metal states were most active for the cobalt, iron, and nickel oxides, while the Cu^+ state was more active than the Cu metal state for the copper oxide.

The investigation of the catalytic reduction of NO by CO has advanced as part of an effort to prevent the air pollution caused by automobile exhaust, for this reaction can simultaneously change two noxious species, that is, nitrogen oxide and carbon monoxide, to innoxious species, that is, nitrogen and carbon dioxide. Many studies of catalyzed reactions over metal oxide catalysts have been reported.[1–4] However, the study of the correlation of the activities of the metal oxide catalysts with their surface states has rarely been reported. Therefore, it would be very interesting to investigate such a correlation. In the NO–CO reaction, great interest is focussed on what the surface states of the catalysts are during the reaction and on what valence states of the metal ions in the catalysts are most active. Accordingly, the surface states of the metal oxides were studied with ESCA in an attempt to solve these problems.

The phenomenon that the surface of the catalysts was reduced after the NO–CO reaction was observed, so the metal oxides were treated with CO gas in order to reduce them to some degree. Subsequently, the surface states of those reduced oxides were studied with ESCA in order to investigate the correlation of the activities of the catalysts for the NO–CO reaction with the surface states of the catalysts, and also the correlation of their surface states with the degree of reduction of the bulk catalysts.

Experimental

Fe_2O_3, Co_2O_3, Ni_2O_3, and CuO were used as metal oxide catalysts. The Co_2O_3 and Ni_2O_3 were supplied by Nakarai Chemicals, Ltd., while the CuO was supplied by Wako Pure Chemical Industries, Ltd. Only the Fe_2O_3 was prepared by the decomposition, at 600 °C for 4 h in air, of $Fe(OH)_3$, which had itself been produced from iron(III) nitrate and aqueous ammonia. The BET surface areas of Fe_2O_3, Co_2O_3, and Ni_2O_3 were 4.7, 24.8, and 141.3 m^2/g respectively.

The reduction of these catalysts and the reactions between CO and NO were carried out in a usual closed circulating system apparatus, the volume of which was about 340 cm^3. The amount of the catalyst used in each run was 0.020 g for Co_2O_3, Ni_2O_3, and CuO, and 0.100 g for Fe_2O_3. The catalyst, set in the closed circulating apparatus, was evacuated for 4 h at 400 °C, and then it was reduced by CO for a given time at 300 °C. Subsequently, after the evacuation, a reactant gas was introduced into the system, and the reaction between CO and NO was carried out at 300 °C. The partial pressures of NO, CO, and Ar in the gas mixture at about 4.7 cmHg were 1.8, 1.9, and 1.0 cmHg respectively. The product gas mixture was analyzed by means of a Hitachi RMS-4 mass spectrometer calibrated for pure gases. The concentrations of the product gas constituents (CO_2, N_2, and so on) were calculated by comparing their peak intensities with that of Ar. The reaction rates were calculated from the rates of the increases in the peak intensity at $m/e=44$.

The degree of reduction of the bulk catalysts, which is represented by x, is defined by the ratio of the amount of oxygen in the catalyst lost by reduction to that of oxygen in the catalyst before reduction. That is, $M_2O_{3(1-x)}$ shows the composition of the bulk at x for sesquioxides, and $MO_{(1-x)}$, that for monoxides. The conversion of CO into CO_2 was estimated by means of analysis with the mass spectrometer. The CO disproportionation ($2CO \rightarrow CO_2 + C$) occurred at the same time in the reduction by CO. The extent of the disproportionation can be estimated by the amount of the pressure decrease in the closed system. Thus, the above reduction degree was corrected.

The photoelectron spectra were measured on a Hitachi 507 photoelectron spectrometer using Al $K\alpha_{1,2}$ radiation. Powdered samples were mounted on a sample holder made of stainless steel. The oxide catalysts were reduced by CO in a closed treatment chamber which was directly linked to the analysis part. After evacuation, the reduced catalysts were immediately introduced into the adjacent analysis part and were measured with ESCA. Also, in this case the reduction degree was determined in the same way as in the above closed circulating system. The binding energies were corrected by using the value of 285.0 eV for the C 1s level resulting from the contaminated carbon. The reproducibility of this value was within ±0.2 eV.

Results and Discussion

Figure 1 shows the dependence of the initial reaction rate on the degree of reduction of the catalysts. Initial reaction rates were used to represent the activity, since the catalysts were reduced by the progress of the reaction. Figure 1 indicates that the activities increase as the degree of reduction increases for three oxides of Fe,

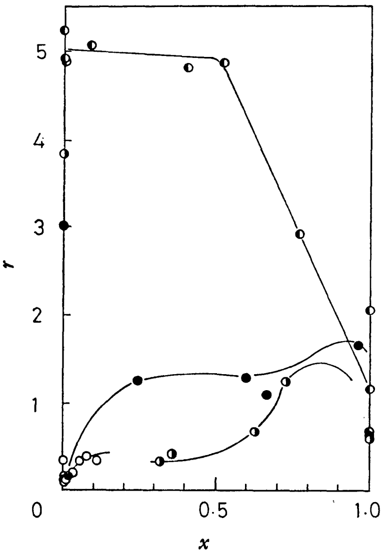

Fig. 1. Dependence of the initial reaction rate on the degree of the reduction.
x: Degree of reduction; $M_2O_{3(1-x)}$ for Fe, Co, and Ni; $MO_{(1-x)}$ for Cu.
r: Initial reaction rate (cmHg/min·g)
●: Co_2O_3, ○: Fe_2O_3, ◑: Ni_2O_3, ◐: CuO

Co, and Ni, and that no very marked change occurs at a moderate degree of reduction (x=0.2—0.6) for the cobalt oxide. The oxides of Co and Ni have comparably high activities near the degree of x=1. That is, they are supposed to have high activities near the metal state. At the degree of x=1, the oxides of both Co and Ni have low activities; this may be caused by the deposited carbon produced by the incidental CO disproportionation. The oxides of Co and Ni, which were not reduced before the reaction, have considerably high activities. These high activities are considered to be attributable to the excess oxygen adsorbed originally on the surfaces of the oxides used. That is, in the case of these catalysts, CO rapidly reacts with the excess oxygen in the initial stage of the reaction; hence, the formation of CO_2 increases upon the additional reaction. Therefore, the activities are considered to be very high.

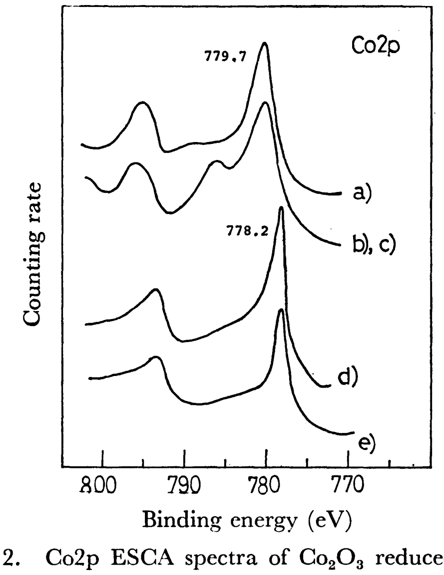

Fig. 2. Co2p ESCA spectra of Co_2O_3 reduced by CO. a) x=0, b) x=0.37, c) x=0.65, d) x=0.99, e) x=1.

The behavior of the copper oxide is markedly different from the other three oxides. In Fig. 1 the curve for the copper oxide shows a break at the degree of x=0.5; below this point a high activity is maintained. while above it the activity descends linearly with the degree of reduction. It is obvious that the activity of the copper oxide is higher than those of the other three oxides used in almost all the range of the degrees of reduction.

TABLE 1. ASSIGNMENT OF THE ESCA SPECTRA OF THE METAL OXIDES IN FIGS. 2, 4, 5, AND 7

Oxide	Spectra	x (Degree of reduction)	Bulk constituent	Surface species
Co_2O_3	a)	0	$CoO_{1.5}$	Co^{3+}
	b)	0.37	$CoO_{0.95}$	Co^{2+}
	c)	0.65	$CoO_{0.53}$	Co^{2+}
	d)	0.99	$CoO_{0.02}$	Co^0
	e)	1	Co	Co^0
Fe_2O_3	a)	0	$FeO_{1.5}$	Fe^{3+}
	b)	0.04	$FeO_{1.44}$	Fe^{3+}, Fe^{2+}
	c)	0.11	$FeO_{1.33}$	Fe^{3+}, Fe^{2+}
Ni_2O_3	a)	0	$NiO_{1.5}$	Ni^{2+}
	b)	0.52	$NiO_{0.72}$	Ni^{2+}
	c)	0.58	$NiO_{0.63}$	Ni^{2+}, Ni^0
	d)	0.74	$NiO_{0.39}$	Ni^{2+}, Ni^0
CuO	a)	0	CuO	Cu^{2+}
	b)	0.02	$CuO_{0.98}$	Cu^{2+}
	c)	0.16	$CuO_{0.84}$	Cu^{2+}, Cu^+
	d)	0.40	$CuO_{0.60}$	Cu^+
	e)	0.76	$CuO_{0.24}$	Cu^0

Then we studied, by means of ESCA, the correlation of the surface states of the metal oxides with the reduction degree of the bulk oxides. Figure 2 shows the ESCA spectra of Co 2p for the cobalt oxide. The a), b), and c) spectra in Fig. 2 roughly correspond to Co_2O_3, CoO, and $CoO_{0.5}$ respectively in terms of bulk. Therefore, both the d) and e) spectra correspond to the metal state in bulk. The assignment of the spectra of the cobalt oxide and of the other metal oxides is shown in Table 1. In Fig. 2, it may be observed that the b) spectrum is the same as the c) spectrum, though the degree of the bulk reduction of the former (x=0.37) is different from that of the latter (x=0.65). The b) and c) both spectra correspond to CoO.[5] From these facts it may be considered that the surface state of the cobalt oxide remains CoO over a considerably wide range of the degree of reduction and that the oxygen in the surface layer is richer than in the bulk at a moderate degree of reduction. This fact is consistent with the constant activity at a moderate degree of reduction for the cobalt oxide in Fig. 1. Figure 3 shows the dependence of the peak intensities of O1s and C1s on the cobalt oxide surface upon the degree of reduction. This dependence agrees well with the above facts that the intensity of the O1s peak on the surface is constant at a moderate degree of reduction. When the cobalt oxide at the degree of x=1 was further reduced, it was found

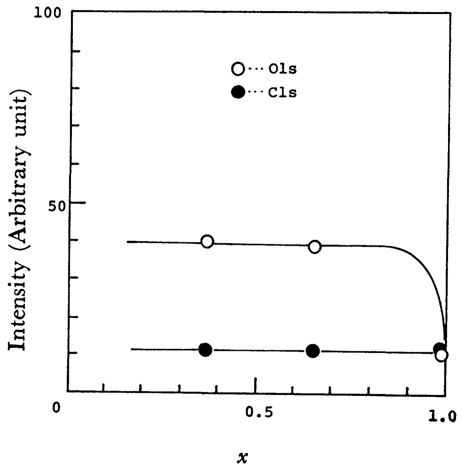

Fig. 3. Dependence of the peak intensity of O1s and C1s for Co_2O_3 on the degree of reduction.
x: Degree of reduction.

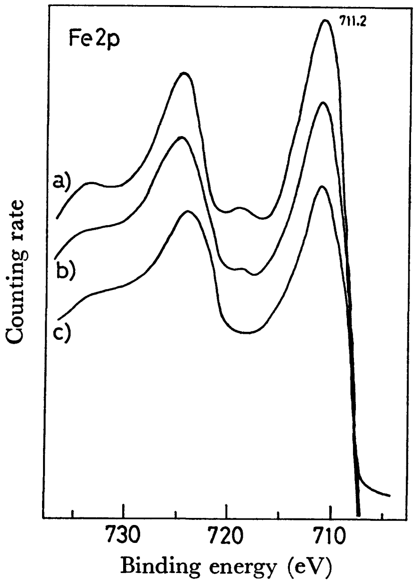

Fig. 4. Fe 2p ESCA spectra of Fe_2O_3 reduced by CO.
a) $x=0$, b) $x=0.04$, c) $x=0.11$.

that the intensity of the C1s peak on the cobalt surface increased suddenly; this suggests that the disproportionation of CO occurs when the oxygen in the cobalt oxide is exhausted.

Fe_2O_3 is more difficult to reduce than Co_2O_3. The spectra of the iron oxide show no remarkable change, as is shown in Fig. 4, but the main peaks of Fe2p tend to become broader and its satellite peaks disappear as the oxide is reduced. It may be supposed that the spectra accompanied by the satellite peaks correspond to Fe^{3+} and that the spectra without them correspond to the mixed state of Fe^{2+} and Fe^{3+} in Fe_3O_4. Therefore, it may be concluded that, in the case of the iron oxide, the divalent and trivalent states of iron can not definitely be differentiated on the basis of the Fe 2p-spectral data.

As is shown in Fig. 5, the spectra of Ni 2p vary around the degree of $x=0.5$. It may be considered from Fig. 5 that the surface constituent of the nickel oxide is NiO below the degree of $x=0.5$ and is a mixture of NiO and nickel metal above the degree of $x=0.5$. Figure 6 shows the dependence of the intensity of the O1s and C1s spectra for the nickel oxide surface on the degree of reduction. The amount of the surface oxygen is roughly constant below the degree of $x=0.5$, while it decreases sharply near the degree of $x=0.5$; this coincides with the above reduction tendency of the nickel oxide. Figure 1 indicates that the activity of the nickel oxide is roughly constant below the degree of $x=0.5$ and increases above the degree of $x=0.5$; this increase in the activity corresponds with the appearance of nickel metal on the catalyst surface. Thus, the behavior of the nickel oxide is similar to that of the cobalt oxide, except that the former produces the metal states at a lower reduction degree than does the latter.

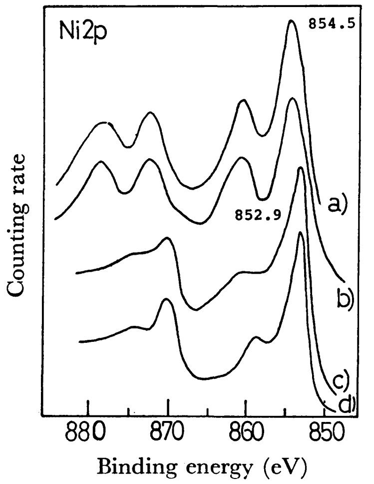

Fig. 5. Ni 2p ESCA spectra of Ni_2O_3 reduced by CO.
a) $x=0$, b) $x=0.52$, c) $x=0.58$, d) $x=0.74$.

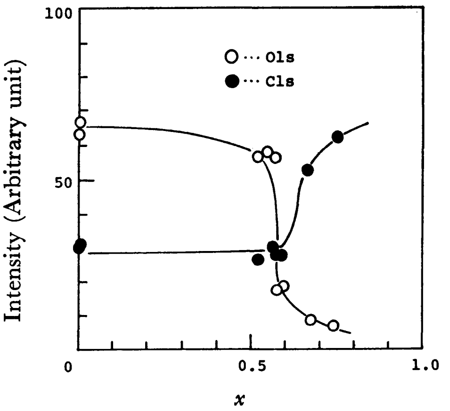

Fig. 6. Dependence of the peak intensity of O1s and C1s for Ni_2O_3 on the degree of reduction.
x: Degree of reduction.

In Fig. 5, the a) spectrum at the degree of $x=0$ after the evacuation treatment, which is accompanied by satellite peaks, may be supposed to correspond to the Ni^{2+} state in spite of the Ni^{3+} bulk constituent, but the binding energy of the Ni $2p_{3/2}$ peak of the spectrum (854.5 eV) is considerably smaller than that of NiO (855.4 eV). This finding suggests that the surface of the oxide may be almost covered with the noncrystal

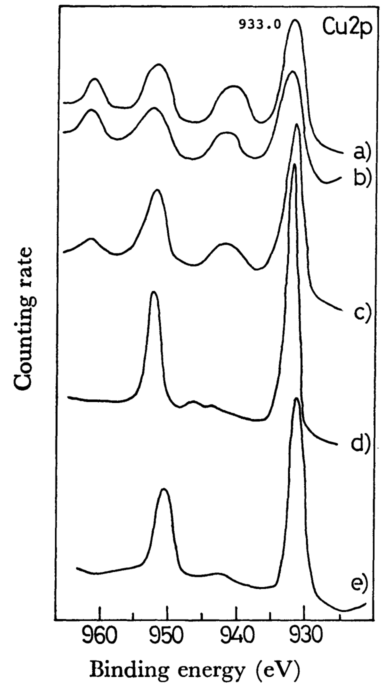

Fig. 7. Cu 2p ESCA spectra of CuO reduced by CO.
a) $x=0$, b) $x=0.02$, c) $x=0.16$, d) $x=0.40$, e) $x=0.76$.

Ni^{2+} oxide with defects upon evacuation at a high temperature.

Figure 7 shows the ESCA spectra of Cu 2p for the copper oxide, while the Cu LMM Auger spectra are shown in Fig. 8. The spectra of Cu 2p start to vary around the degree of $x=0.16$, and the satellite peaks almost disappear at the degree of $x=0.40$, as is shown in Fig. 7. The a) and b) spectra, with the satellite peaks, are assigned to the Cu^{2+} state.[6] In Fig. 7, the ESCA d) spectrum is almost the same as e), while, as is shown in Fig. 8, the kinetic energy of the $L_3M_{4,5}M_{4,5}$ peak of the corresponding Auger spectrum, d), is smaller than that of e) by 1.8 eV. Accordingly, the ESCA spectra in Fig. 7, d) and e), can be assigned to the Cu^+ and Cu metal states respectively.[7] This fact indicates that CuO on the oxide surface may decrease as Cu_2O increases below the degree of about $x=0.40$, and that CuO may almost disappear at the degree of $x=0.40$. Therefore, it may be supposed that the copper oxide catalyst has a high activity when CuO coexists with Cu_2O on the catalyst surface, and that the activity decreases as the copper metal increases above the degree of about $x=0.5$, where CuO disappears entirely. In conclusion, for the copper oxide the active species in the NO–CO reaction is mainly Cu^+, and the Cu metal is a much lower active species than Cu^+.

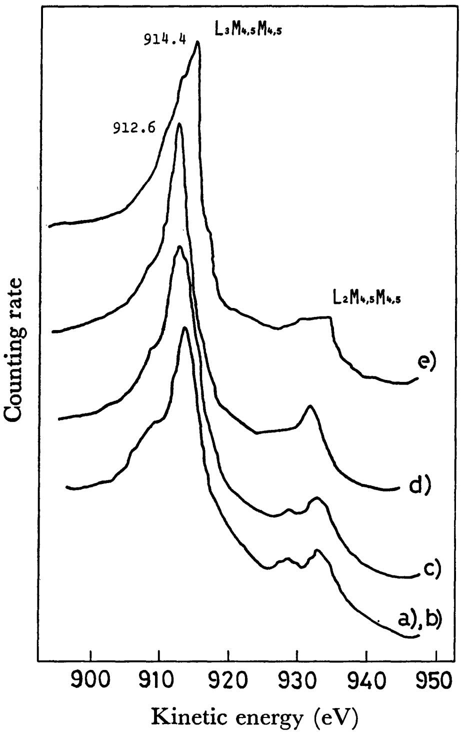

Fig. 8. Auger spectra of CuO reduced by CO.
a) $x=0$, b) $x=0.02$, c) $x=0.16$, d) $x=0.40$, e) $x=0.76$.

It may be concluded that, in the NO–CO reaction, the metal states are most active for the cobalt, iron, and nickel oxides, while the Cu^+ state is more active than the Cu metal state for the copper oxide. As has been mentioned above, the differences between the bulk constituents and the surface states of some reduced metal oxides were revealed by ESCA. Moreover, the correlation between the surface states and the activities of those metal oxides was successfully explained. By using ESCA, useful information on the above problem could also be obtained for other metal compounds which are not dealt with in this paper.

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